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Process for making DAPBI-containing aramid crumbs

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## PROCESS FOR MAKING DAPBI-CONTAINING ARAMID CRUMBS

The invention relates to a method for obtaining a composition comprising an aromatic polyamide containing para-phenylene terephthalamide and 2-(p-phenylene)benzimidazole terephthalamide units by copolymerizing para-phenylenediamine (PPD), 5(6)-amino-2-(p-aminophenyl)benzimidazole (DAPBI);  
5 and terephthaloyl dichloride (TDC) in a mixture of N-methyl pyrrolidone (NMP) and calcium chloride, and to said composition. The invention further relates to a method for making purified aromatic polymer from said composition.

10 Methods for making aramid polymers are known in the art. For instance, in US 4,172,938 an aromatic polyamide was described by polymerizing a mixture of diamines and an aromatic dicarboxylic acid dihalide in a mixture of N-methyl pyrrolidone and calcium chloride. In example 34 of this reference the polymerization reaction is performed with a mixture of para-phenylene diamine  
15 (PPD) and 5-amino-2-(p-aminophenyl)benzimidazole (DAPBI), and terephthaloyl dichloride (TDC) in N-methyl pyrrolidone (NMP) containing 2 wt.% of calcium chloride ( $\text{CaCl}_2$ ). The product was obtained as a powdery clay-like materials for which filtration was problematical. It was disclosed that products according to this reference in more general terms are obtained as slurry, paste, powder, or agar.

20 It is an object of the present invention to provide condition for performing such reaction and obtaining a composition in the form of a crumb or a crumb-like material. The term crumb or crumb-like as used in this invention means that the polymer mixture contains breakable clumps or particles, which are not sticky and  
25 have a mean particle size greater than 100  $\mu\text{m}$ , usually greater than 1 mm.

Such crumbs are known from the process of preparing of fully aromatic polyamides based on e.g. PPD and TDC, which products are known under the trade names Twaron® (Teijin Twaron) and Kevlar® (DuPont). After polymerization in NMP/ $\text{CaCl}_2$   
30 a crumb is obtained which can be easily coagulated, washed, and dried, and the product obtained can be dissolved in sulfuric acid and shaped into a desired form, like fibers or films.

The monomer of interest, DAPBI (5(6)-amino-2-(p-aminophenyl)-benzimidazole; CAS reg. no: 7621-86-5), is added to the diamine mixture with the objective to obtain a suitable polymer solution right after polymerization with e.g. PPD and TDC, which can be directly shaped into fibers or films, whereby DAPBI is seen as a suitable co-monomer to keep the aramid polymer in solution. It was now found that by selecting a specific ratio of PPD, DAPBI, and  $\text{CaCl}_2$  the formation of powders, paste, dough, and the like could be prevented.

To this end the invention relates to a method for obtaining a composition comprising an aromatic polyamide containing para-phenylene terephthalamide and 2-(p-phenylene)benzimidazole terephthalamide units by copolymerizing:

- i) a mole % of para-phenylenediamine (PPD);
- ii) b mole % of 5(6)-amino-2-(p-aminophenyl)benzimidazole (DAPBI); and
- iii) 90-110 mole% of terephthaloyl dichloride (TDC)

in a mixture of N-methyl pyrrolidone and containing c wt.% of calcium chloride, wherein c is within the range from 1 to 20, and wherein the ratio a : b ranges from 1 : 20 to 20 : 1, a + b is 100 mole%, and i), ii), and iii) together comprise 1-20 wt.% of the mixture, characterized in that the product b.c is less than 215 and that the composition is a crumb with a relative viscosity  $\eta_{\text{rel}}$  of at least 4.

It is one of the other objectives of the present invention to obtain crumbs comprising a polymer with a sufficient high relative viscosity  $\eta_{\text{rel}}$ . Relative viscosities  $\eta_{\text{rel}}$  of at least 4, more preferably between 4 and 7, most preferably at least 5 can be obtained according to the method of the invention.

In another object of the invention a method for obtaining a purified aromatic polyamide is obtained by coagulating and washing the obtained crumb with water, followed by drying. The drying step can be performed according to standard procedures, such as ambient conditions, or at elevated temperature and/or lowered pressure. The thus obtained material is suitable for making a spin dope by dissolving it in a solvent, for instance sulfuric acid,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4/\text{CaCl}_2$ ,  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ , and the like. The spin dope can be used to manufacture fibers and films.

### General polymerization procedure

5 DAPBI (ex Spektr T.T.T., Russia) was dried under vacuum for 1 h at 160° C. PPD (Teijin Twaron), TDC (freshly distilled), NMP/CaCl<sub>2</sub> and NMP (both ex Teijin Twaron) were used as received (moisture content 80 ppm).

10 The glassware was pre-dried for 1 h in an air circulation oven at 120° C. A clean and dry 2 l flask was supplied with a mechanical stirrer, N<sub>2</sub>-inlet and outlet, and vacuum supply. Generally, the N<sub>2</sub>-stream is between 40 – 60 ml/min. A large part (400 ml) of the solvent and the precisely pre-weighed amines were carefully brought in the reactor. The reactor was closed and purged two times with nitrogen. The mixture was stirred for 30 min at 150 rpm and heated to 60° C and mixed for 0.5 h to dissolve or disperse the amines properly.

15 The flask was cooled with ice/water to 5 – 10° C. After removing the coolant, the stirrer velocity was set at 320 rpm and a precisely pre-weighed amount of the acid chloride was brought into the vessel through a funnel. In all cases the mol ratio of the total number of amines and the acid chloride equals one. The flask, which contained the acid chloride and the funnel, were rinsed with the remaining solvent  
20 (50 ml). The vessel was closed and the mixture was allowed to react for at least 30 min (nitrogen flush between 40 – 60 ml/min). The stirring was stopped and the reaction vessel was removed.

25 The crumbed product together with demi-water was gently added into a Condux LV15 15/N3 coagulator and the mixture was collected on an RVS filter. The product was washed 4 times with 5 l of demi-water, collected in a 2 l glass beaker and dried under vacuum for 24 h at 80° C.

30 A sample was dissolved in sulfuric acid at room temperature. The flow time of the sample solution in sulfuric acid 96% (0.25 % m/V) was measured at 25° C in an Ubbelohde viscometer. Under identical conditions the flow time of the solvent was measured as well. The relative viscosity was then calculated as the ratio between the two observed flow times.

### Results

After addition of the TDC, the temperature increased rapidly and could reach its maximum between 40° and 70° C.

- 5 The Table shows some examples in which the polymer mixture turned into a crumbed mass, which could easily be coagulated and washed. To obtain crumbs the DAPBI content, monomer concentration, and the  $\text{CaCl}_2$  concentration must be balanced according to the invention.
- 10 In comparative examples I – III the polymer mixture was rendered as a dough polymer mass or as rubbery "chewing gum-like" mass, due to the high  $\text{CaCl}_2$  content. In Example IV first a precipitate was formed, which was later converted to a dough-like mass. The  $\text{CaCl}_2$  content was too low to obtain a crumb. Example V (according to US 4172938) resulted in a powdery material, which after coagulation
- 15 was very difficult to filter. It behaved like a clay-like material.

Table

Examples	PPD a mole%	DAPBI b mole %	$\text{CaCl}_2$ c wt. %	b.c	$\eta_{\text{rel}}$	crumb
1	90	10	10.40	104.0	6.29	yes
2	90	10	11.55	115.5	5.93	yes
3	80	20	9.85	197.0	5.38	yes
4	80	20	10.28	205.6	4.10	yes
5	60	40	4.77	190.8	5.69	yes
6	33	67	3.09	207.0	6.98	yes
7	30	70	2.82	197.4	6.2*	yes
Comparative Examples						
I	80	20	11.55	231.0	4.59	dough/paste
II	60	40	5.49	212.6	5.67	dough/paste
III	33	67	4.53	203.8	2.75	dough/paste

21 Nov. 2003

## Claims:

1. A method for obtaining a composition comprising an aromatic polyamide containing para-phenylene terephthalamide and 2-(p-phenylene)benzimidazole terephthalamide units by copolymerizing:

5 i) a mole % of para-phenylenediamine;

ii) b mole % of 5(6)-amino-2-(p-aminophenyl)benzimidazole; and

iii) 90-110 mole% of terephthaloyl dichloride

in a mixture of N-methyl pyrrolidone and containing c wt.% of calcium chloride,

wherein c is within the range from 1 to 20, and wherein the ratio a : b ranges from

10 1 : 20 to 20 : 1, a + b is 100 mole%, and i), ii), and iii) together comprise 1-20 wt.%

of the mixture, characterized in that the product b.c is less than 215 and that the

composition is a crumb with a relative viscosity  $\eta_{rel}$  of at least 4.

2. A composition comprising an aromatic polyamide containing para-phenylene terephthalamide and 2-(p-phenylene)benzimidazole terephthalamide units, obtainable by copolymerizing para-phenylenediamine; 5(6)-amino-2-(p-aminophenyl)benzimidazole; and terephthaloyl dichloride in a mixture of N-methyl pyrrolidone and calcium chloride, characterized in that the composition is a crumb with a relative viscosity  $\eta_{rel}$  of at least 4.

3. The composition of claim 2 wherein the crumb has a relative viscosity  $\eta_{rel}$  between 4 and 7.

4. A method for making purified aromatic polyamide by coagulating and washing the crumb of claim 2 or 3 in water, followed by a drying step.

21. Nov. 2003

**Abstract**

The invention pertains to a method for obtaining a composition comprising an aromatic polyamide containing para-phenylene terephthalamide and 2-(p-phenylene)benzimidazole terephthalamide units by copolymerizing:

i) a mole % of para-phenylenediamine (PPD);

5 ii) b mole % of 5(6)-amino-2-(p-aminophenyl)benzimidazole (DAPBI); and

iii) 90-110 mole% of terephthaloyl dichloride (TDC),

in a mixture of N-methyl pyrrolidone and containing c wt.% of calcium chloride,

wherein c is within the range from 1 to 20, and wherein the ratio a : b ranges from 1 : 20 to 20 : 1, a + b is 100 mole%, and i), ii), and iii) together comprise 1-20 wt.%

10 of the mixture, characterized in that the product b.c is less than 215 and that the composition is a crumb with a relative viscosity  $\eta_{rel}$  of at least 4, preferably between 4 and 7.